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Absorption spectra of broadened sodium resonance lines in presence of rare gases

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Abstract. The pressure broadening of alkali-metal lines is a fundamental problem with numerous applications. For example, the sodium resonance lines broadened by xenon are important in the production of broad spectra emitted in the HPS (High-Pressure Sodium) lamp and they potentially can be used for gas condition diagnostics. Broadened absorption lines of alkali-metal atoms are prominent in the optical spectra of brown dwarfs and understanding the broadening mechanism will help elucidate the chemical composition and atmospheric properties of those stars.

The far-line wing spectra of sodium resonance lines broadened by rare gases are found to exhibit molecular characteristics such as satellites and hence the total absorption coefficients for vapors of Na atoms and perturbing rare gas atoms can be modeled as Na-RG (rare gas) molecular absorption spectra. In this work, using carefully chosen interatomic potentials for Na-RG molecules we carry out quantum-mechanical calculations for reduced absorption coefficients for vapors composed of Na-He, Na-Ar, and Na-Xe. Calculated spectra are compared to available experimental results and the agreement is good in the measured satellite positions and shapes.

INTRODUCTION

Line broadening of sodium resonance lines in presence of perturbing atoms have been extensively studied over several decades. Due to interatomic interaction between Na atom and perturbers, far line wings of the broadened lines exhibit characteristics of molecular spectra. Therefore, experimental methods such as laser-induced fluorescence, emission and absorption spectroscopy have been used to study properties of interatomic interactions such as interaction potentials. In addition to the fundamental studies of molecular physics, thermal emission and absorption spectra of sodium resonance lines are studied in the context of various applications such as the modeling of high-pressure sodium lamps and optical diagnostics of combustion and chemical reactions.

Theoretically, the far line wing spectra has been studied with classical and semi-classical methods. These methods give a good description of gross features of absorption and emission spectra. However, recent high-precision measurements of absorption coefficients [1] reveal more detailed features such as ro-vibration lines and satellite structures in the far line wings of sodium resonance lines when broadened by the same or different perturbing atoms requiring more precise theoretical descriptions. Accurate quantum-mechanical methods in molecular spectroscopy are not usually applied to the spectral calculations for high temperature gas partly because the uncertainty of available molecular potentials is comparable to that of the classical and semi-classical methods and partly

TABLE 1. Molecular potentials used in the calculations

| Rare gas | $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ potentials |
|----------|---|
| He | Theodorakopoulos and Petsalakis [8] |
| Ar | Kerner <i>et al</i> [9] |
| Xe | Baumann <i>et al.</i> ($X^2\Sigma^+$ and $A^2\Pi$) [10] Düren-type potential function ($B^2\Sigma^+$) [11, 7] |

because of the computational limitations resulting from the difficulty of accounting for all the partial waves contributing to the total spectra. Recently, however, accuracies for atomic and molecular data have been greatly improved by utilizing various methods such as laser spectroscopy, photoassociation spectroscopy, Feshbach resonance, and ultracold collisions, and also recent advances in computer speed and techniques of parallel and distributed processing made it possible to consider the convergent number of partial waves involved in calculations. In this work, using the PVM (Parallel Virtual Machine) technique, we carry out quantum-mechanical calculations of absorption coefficients for far line wing spectra of sodium resonance lines broadened by rare gases.

QUANTUM-MECHANICAL METHOD

When broadened by rare gases, absorption coefficients of sodium resonance lines arising from $3s$ to $3p$ transitions can be modeled as molecular spectra of transitions within di-molecules composed of sodium and rare gas atoms. Absorption transitions occur from the lower molecular states which approach the absorbing sodium ($3s$) and the perturbing rare gas atomic states at a long-range limit to the upper molecular states which approach the excited sodium ($3p$) and the spectator rare gas atomic states. Depending on whether the molecular potentials have bound states formed by sodium and rare gas atoms, the total spectra consist of four possible transitions; bound-bound, bound-free, free-bound, free-free transitions. Details of quantum-mechanical formulation of each transition are described in our earlier papers [2, 3].

Most important are the molecular potentials involved in the radiative transitions and a lot of care was taken into using the most accurate molecular potentials of sodium-rare gas di-molecules. Molecular potentials are roughly divided into short-range potentials which can be obtained by *ab initio* calculations or experimental methods such as laser spectroscopy or line broadening measurements and long-range potentials normally described as $V(R) = -C_6/R^6$ where van der Waals forces are dominant. We investigated the potentials available in the literature by calculating theoretical values of thermal gas parameters such as diffusion coefficients and index of refraction of sodium matter waves using those potentials and comparing with the measured values [4, 5]. Measured satellite positions [1, 6, 7] were applied to select and modify molecular potentials as well. Molecular potentials of our choice are listed in Table. 1–2 for Na-He and Na-Ar and Na-Xe molecules. Details of our studies on molecular potentials will be published elsewhere shortly [7].

TABLE 2. C_6 values in atomic units for long-range molecular potentials $V(R) = -C_6/R^6$ used in calculations

| Rare gas | $X^2\Sigma^+$ potential | $A^2\Pi$ potential | $B^2\Sigma^+$ potential |
|----------|-------------------------|--------------------|-------------------------|
| He | 26.2 [12] | 49.2 [13] | 71.4 [13] |
| Ar | 190.0 [12] | 534.7 [9] | 717.8 [9] |
| Xe | 455.9 [12] | 897.4 [14] | 1095.4 [14] |

COMPARISONS WITH MEASUREMENTS

Experimentally, the absorption coefficients of sodium vapor at $900(^+10^{-50})\text{K}$ in presence of various rare gases were measured in the range from 400 nm to 850 nm. With the sodium atomic densities obtained accurately using the anomalous dispersion method [1], density-independent reduced absorption coefficients of Na-Na and Na-Rare gases were obtained simultaneously. The measured reduced absorption coefficients (upper curves) for Na-He, Na-Ar and Na-Xe are compared with the calculated values (lower curves) in Fig. 1. The blue wing absorption arises from transitions between the $X^2\Sigma^+$ molecular state to the $B^2\Sigma^+$ molecular state and the red wing from transitions between the $X^2\Sigma^+$ molecular state to the $A^2\Pi$ molecular state. Since the ground electronic states of Na and rare gas di-molecules are weakly bound, most absorption occurs from free-bound and free-free transitions and the absorption spectra should be smooth without ro-vibrational structures¹.

In the blue wings notable features are the primary peaks occurring at 530, 555 and 560 nm for Na-He, Na-Ar and Na-Xe respectively. Quantum-mechanical calculations reproduce the primary peaks at the measured positions. In addition to the primary peaks, there are weaker secondary peaks shown for Na-Ar and Na-Xe and they are also reproduced in calculations. The semi-classical method suggested by Bieniek and Streeter [15, 16] also yields results similar to the quantum-mechanical method, however, other classical and semi-classical methods [17] fail to describe the primary and the secondary peaks altogether. While our results give a overall good agreement, we found that the absolute values of calculated intensities are slightly lower than the measured values and the sources of discrepancies are not known yet. We also found that the secondary peaks require more stringent tests of molecular potentials than primary peaks and the shapes and the positions of the secondary peaks can be applied to refine molecular potentials.

¹ The structures in the experimental red wing spectra are believed to be merely the remnants of sodium dimer spectra appearing because reduced absorption coefficients are extracted from spectra of total absorption coefficients for the gas mixtures.

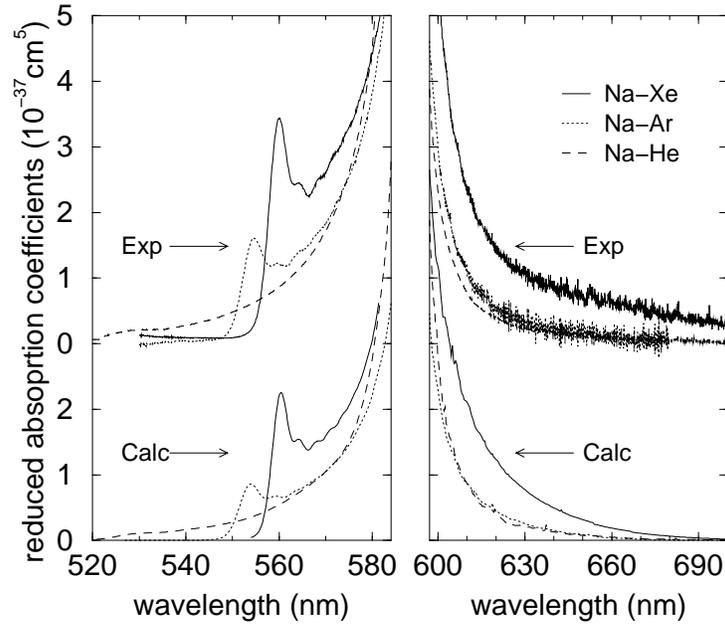


FIGURE 1. Comparisons for Na-rare gas molecules of reduced absorption coefficients between experiment at temperature of $900+10 - 50\text{K}$ (upper curves) and theory at temperature of 900K (lower curves).

APPLICATIONS

Pressure broadening of atomic resonance lines is a key ingredient of various lighting sources. In particular, our research is germane to the spectra of high-pressure sodium lamps [18]. Our measured and calculated absorption coefficients might be utilized for improved emission models.

Another intriguing application of the present research is found in astrophysics. The spectra of brown dwarfs contains alkali-metal atom resonance lines pressure-broadened predominantly by the perturbing gases He and molecular hydrogen [19]. The resonance lines of K and Na are particularly prominent and improved modeling of their broadening may lead to better knowledge of atmospheric composition, effective temperature and gravity [20, 21].

SUMMARY

High precision measurements were used to obtain the absorption spectra of sodium resonance lines in presence of rare gases. The absorption coefficients show interesting peak structures in the blue wings. We demonstrated that quantum-mechanical methods can be applied to describe the peak and the overall features of far wing spectra of sodium resonance lines when broadened by rare gases. Our results show that the structures provide a good test of molecular potentials of sodium-rare gas di-molecules.

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